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13. ABSTRACT (Maximum 200 words) We have studied the structure of amorphous $\text{Ge}_{1-x}\text{Sn}_x\text{Se}_2$ and its photoinduced transformations using Raman and Mössbauer spectroscopies, ellipsometry, optical absorption, and a variety of other techniques. We find that the glass consists of two types of distinct structural units with distinct responses to pressure, and that the Sn atoms preferentially occupy tetrahedral sites at the edges of one of these units. As the Sn concentration is increased the size of the units decreases to provide more edge sites. These structural changes resulting from the addition of Sn cause a decrease in the optical band gap and a suppression of the photodarkening response.			
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FINAL REPORT
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Dr. Laurie E. McNeil, P.I.

Statement of problem

This research project had as its primary focus the structure of GeSe_2 -based glasses and the influence of that structure on the properties of the material. Chalcogenide glasses exhibit a variety of phenomena which do not occur in the corresponding crystal forms, and which must therefore be linked to the disordered structure of the glass. The short-range order of the glass is controlled by the bonding chemistry of these covalent compounds and is very similar to that of the crystal. The behavior unique to the glassy forms arises from the intermediate-range order, which was the object of our study. We were able to fabricate $\text{Ge}_{1-x}\text{Sn}_x\text{Se}_2$ compounds in several forms (bulk glass, evaporated film, bulk crystal) and apply a variety of analytical techniques to study them. These included Raman and Mössbauer spectroscopies, optical absorption, ellipsometry, differential scanning calorimetry, X-ray diffraction, and Rutherford backscattering. The students who participated in this work thus received broad training in materials fabrication and characterization.

The chalcogenide glasses are of scientific and technological interest due to the variety of photoinduced phenomena which occur in them. Two which received attention in this study were *photodarkening* and *photoinduced diffusion*. In the photodarkening process illumination with above-bandgap light induces a decrease in the optical band gap. This shift is stable at room temperature but is reversible upon heating, and could potentially form the basis for an erasable optical memory. Photoinduced diffusion refers to the rapid diffusion of metal atoms into the glass in the presence of light. This phenomenon may have applications in photolithography, and like photodarkening it occurs only in the glassy form of the material. An understanding of both of these behaviors requires a much clearer picture of the glassy structure than was available prior to this study.

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Principal results

The first major result of this work was the elucidation of the molecular cluster network of $\text{Ge}_{1-x}\text{Sn}_x\text{Se}_2$ glass. By using a combination of Raman and Mössbauer spectroscopies at ambient and high pressures and by comparing the spectra of the crystalline and glassy forms we were able to determine that the glass consists of two distinct types of clusters, whose differential response to pressure indicates that they are separate covalently-bonded entities only weakly bonded to one another. This provides conclusive evidence that the glass does not form a continuous random network at any Sn concentration, in contrast to what had previously been proposed. These two entities are sometimes referred to as "clusters" and "chains". We were also able to determine that the substitution of Sn into Ge sites is not random, but rather that for any Sn concentration 85% of the Sn atoms occupy sites of tetrahedral symmetry on the clusters. The remaining 15% of the Sn atoms are located in lower-symmetry sites on the chains. Further, there are two types of tetrahedral sites which can be distinguished by Raman spectroscopy--those in the interior of the cluster, and those on the cluster edges. Due to the strain introduced by the substitution of Sn for Ge, this substitution takes place preferentially on the edges of the clusters. As the Sn concentration is increased, the average size of the clusters decreases so that more edge sites become available for Sn occupation. When the minimum cluster size consistent with the bonding geometry is reached, it becomes impossible to form a homogeneous glass and phase separation occurs. This work is detailed in publications 1, 3, 4, and 8, and formed substantial parts of the Ph.D. dissertations of J.M. Mikrut and M.J. Peters.

Once these structural alterations introduced into the GeSe_2 glass by the addition of Sn were understood, our next task was to study their influence on the properties of the glass, in particular on the photodarkening response. Using optical absorption and ellipsometry we were able to measure the changes in the band gap and index of refraction introduced by the substitution of Sn for Ge. We observed that the optical band gap (E_g) decreased and the index of refraction (n) at 1.96 eV increased as the Sn concentration (x) was increased. We were able to interpret the shape of the E_g vs. x and n vs. x curves in terms of a virtual crystal model, in which the band edges shift rigidly as the states there increasingly take on the character of Sn with its more loosely-bound electrons. An anomaly in the smooth decrease of E_g vs. x curve occurs at the composition for which the cluster breakup described above begins. The microstructure sampled by the Raman and Mössbauer spectroscopies thus controls the electron band states and the optical properties of $\text{Ge}_{1-x}\text{Sn}_x\text{Se}_2$, in a way which we now understand. These results were detailed in publication 7, and formed the major part of the M.S. research of L.W. Martin.

With this understanding of the relation between cluster size and optical band gap, we directed our attention to the photodarkening response. In both the bulk material and the evaporated films the addition of as little as 20% Sn suppressed the photodarkening and led in some cases to slight photobleaching. A variety of factors may contribute to this behavior: shifts in the electron states at the band edges induced by the additional electron density,

smaller cluster size introduced by the presence of significant concentrations of Sn, or steric hindrance associated with the presence of Sn on the cluster edges. Our investigations of intermediate-range order in these glasses show that it is not possible to separate these factors, so that the detailed nature of the photodarkening response remains a complicated problem. The evaporated films also display a curious bleaching effect induced by thermal cycling. This finding, which remains unexplained, recently received independent confirmation [D. Islam, private commun.]. These results were included in the M.S. thesis of Boyd Faulkner, the Ph.D. dissertation of J.M. Mikrut and the B.S. Honors Project of G.B. Turpin, and were reported in publications 2 and 5.

We also investigated the photoinduced diffusion of Ag in GeSe₂ using Rutherford backscattering (RBS) to determine the depth to which Ag evaporated on the surface of the GeSe₂ penetrated into the glass when illuminated. We compared the diffusion depths for identical conditions in bulk glasses and evaporated films, and determined that the diffusion in the films is much faster than that in the bulk glass. This most likely arises from the additional disorder present in (unannealed) films, which can also be observed in the decreased slope of the optical absorption vs. energy curve. More detailed study of diffusion in films showed that the depth profile of the Ag diffused into the GeSe₂ has a Gaussian shape, indicating that the process is diffusion-limited. This finding rules out reaction-limited models in which a well-defined Ag front propagates through the glass. We also observed that although above-bandgap light was far more effective in inducing diffusion than was light of lower energy, if enough total energy was deposited at longer wavelengths a large penetration depth could be achieved. This is similar to the behavior of the light-induced ESR signals observed in these materials, and indicates that the controlling parameter for the diffusion is the total energy absorbed rather than the wavelength of the light. This work was the M.S. research of Steven Bozeman.

In the course of this project it was necessary to eliminate any effects that might have resulted from the presence of crystalline species within the glass. This led us to undertake a Mössbauer study of crystalline SnSe as a function of pressure, as a coincidence in the isomer shifts of Ge_{1-x}Sn_xSe₂ and SnSe at ambient pressure led us to suspect that small amounts of SnSe might be present in our amorphous samples and give rise to the observed pressure behavior. Our study of SnSe, which is detailed in publication 6, demonstrated that this crystalline material could in no way be responsible for our Ge_{1-x}Sn_xSe₂ results. The sign and magnitude of the pressure dependence of the isomer shift in SnSe is completely different from what we observed in the ternary glass.

Scientific personnel

Six students (five graduate students and one undergraduate) were involved in the research described above. Their names, degree dates and present whereabouts are as follows:

Boyd Faulkner (M.S. 1987): employed in industry.

John Mikrut (M.S. 1987, Ph.D. 1989): postdoctoral associate at Northwestern Univ.

G. Bradley Turpin (B.S. honors project 1989): graduate student in physics at Ohio State Univ.

Lawrence Martin (M.S. 1989) completed his Ph.D. in solid state theory with another research group, now on the faculty at North Park College (Chicago).

Steven Bozeman (M.S. 1990): pursuing his Ph.D. in a plasma physics research group at UNC.

Marian Peters (Ph.D. 1990): postdoctoral associate with the Free Electron Laser project at Duke Univ.

Publications

1. "Phase separation in $\text{Ge}_{1-x}\text{Sn}_x\text{Se}_2$ glasses", L.E. McNeil, J.M. Mikrut and M.J. Peters, *Solid State Commun.* **62**, 101 (1987).
2. "Photodarkening in amorphous $\text{Ge}_{1-x}\text{Sn}_x\text{Se}_2$ films", G.B. Turpin and L.E. McNeil, *Phys. Rev. B* **39**, 8750 (1989).
3. "Fragmentation of the molecular cluster network of amorphous $\text{Ge}_{1-x}\text{Sn}_x\text{Se}_2$ ", J.M. Mikrut and L.E. McNeil, *J. Non-Crystalline Solids* **109**, 237 (1989).
4. "Intercluster and intracluster interactions in $\text{Ge}_{1-x}\text{Sn}_x\text{Se}_2$ ", L.E. McNeil and M.J. Peters, *J. Non-Crystalline Solids* **114**, 64 (1989).
5. "Photostructural changes in bulk amorphous $\text{Ge}_{1-x}\text{Sn}_x\text{Se}_2$ ", J.M. Mikrut and L.E. McNeil, *J. Non-Crystalline Solids* **114**, 127 (1989).
6. "High-pressure Mössbauer study of SnSe ", M.J. Peters and L.E. McNeil, *Phys. Rev. B* **41**, 5893 (1990).
7. "Index of refraction and optical absorption in amorphous $\text{Ge}_{1-x}\text{Sn}_x\text{Se}_2$ ", L.W. Martin, L.E. McNeil and J.M. Mikrut, *Phil. Mag. B* **61**, 957 (1990).
8. "Evidence of distinct structural clusters in amorphous $\text{Ge}_{1-x}\text{Sn}_x\text{Se}_2$ ", M.J. Peters and L.E. McNeil, *J. Non-Crystalline Solids* [in press] (1992).